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Estimation of oxygen concentration in the slurry in biogas production without O_2 removal in initial process

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Abstract

The existence of free molecular oxygen in the biogas production process will inhibit strict anaerobic methanogenic bacteria. The estimation of O_2 concentration in the slurry is needed to see if the oxygen methanogenic inhibition happens in the biogas production without oxygen removal in initial process. The calculation begin with determine the digester volume, the gas space volume fraction in the digester, and the operation condition, i.e. the temperature and the pressure according to the good condition in the biogas production process. Based on the liquid-gas equilibrium principle, and with the assumption that the air consist of 80% of nitrogen and 20% of oxygen, it is obtained the equilibrium oxygen concentration in the slurry in various gas space volume fraction in the digester. The result of the calculation show that the oxygen concentrations in the slurry in all of gas space volume fraction in the digester are much higher than the methanogenic inhibition limit, indicating the possibility the happen of the methanogenic inhibition in the system. The inhibition possibility will be higher by the greater of the gas space volume fraction in the digester.

Key words: Oxygen concentration; biogas production; O_2 removal; methanogenic inhibition; liquid-gas equilibrium principle; gas space volume fraction

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1. Introduction

Biogas production process is the process that converts organic compounds to biogas, mainly containing of CH_4 and CO_2 [1]. The processes are done by various anaerobic bacteria to obtain energy for their growth. There are very complex process, but according to Rittmann and McCarty (2001) can be broken into two basic steps, as illustrated in Equation 1 [2]:

$$\begin{array}{c}\text{Complex}\\ \text{Organics}\end{array} \xrightarrow[\text{Fermentation}]{\text{Hydrolisis +}} \begin{array}{c}\text{Organic acids +}\\ \text{hydrogen}\end{array} \xrightarrow[\text{Formation}]{\text{Methane}} \begin{array}{c}\text{Methane +}\\ \text{Carbon dioxide}\end{array} \qquad (1)$$

The process begins with the bacteria that hydrolyze complex organic matter such as carbohydrates, proteins, and fats into simple carbohydrates, amino acids, and fatty acids [2]. The simple organic matter are the monomer of complex organic compounds, and become major electron donors for energy methabolism [3]. These simple compounds are then utilized by fermenting bacteria, producing organic acids and hydrogen as the dominant intermediate products. The organic acids are then partially oxidized by other fermenting bacteria, which produce additional hydrogen and acetic acid. Hydrogen and acetic acid are the main substrates used by methanogens, which convert them into methane [2].

The bacteria in hydrolysis step are facultative and obligatorily anaerobic bacteria[4], and the majority of the acidifying bacteria (acid forming bacteria) are facultatively anaerobic [4, 5]. Facultatively anaerobic bacteria are active in the presence or absence of free molecular oxygen [6]. The methanogenic bacteria are strict anaerob [5,6], that will die in the presence of free molecular oxygen [6]. The oxygen inhibition of methanogenic bacteria begins at 0.1 mg/L O_2 [4]. The biogas production process is always operated in anaerobic condition because involving strict anaerobic methanogenic bacteria. To ensure the complete anaerobic condition, usually the air in the gas space in the digester in initial process is removed by flushing inert gas or making the vacuum condition [7]. If the biogas process can run well without oxygen removal, the operation cost may be reduced. This research is purposed to estimate the equilibrium oxygen concentration in the slurry in biogas production without oxygen removal in initial process. The obtained values are then compared with the oxygen methanogenic inhibition limit, so that it can be seen if the oxygen methanogenic inhibition possibly happens in the system. This research is the preliminary research to know the possibility the happen of the methanogenic inhibition caused by the existence of air (containing free molecular oxygen) in the digester gas space in initial process.

2. Analysis Method

Analysis begin with describe the anaerobic digestion system. Fig 1 shows anaerobic digestion integration in the dairy waste stream according to Burke (2001) [8]. The system to be analized is the digester, in where the anaerobic digestion occurs. Biogas digester is a closed reactor (closed tank) containing slurry as microbial growth medium and above the slurry is the gas space to release the biogas formed and to keep the safety of the digester. The digester volume is V liters, and the gas space volume fraction is a, representing the ratio of gas space volume in the digester to total digester volume. In the initial process the gas space is filled with the air from the environment. The biogas digester is described in Figure 2.The oxygen concentration in the slurry will be calculated based on the gas-liquid equilibrium principle. The design variables are the pressure and the temperature recpectively about 1 atm and 30^{o}C, as the good condition for anaerobic bacteria to grow. The air in the environment is assumed consist of oxygen about 20% and nitrogen about 80%.

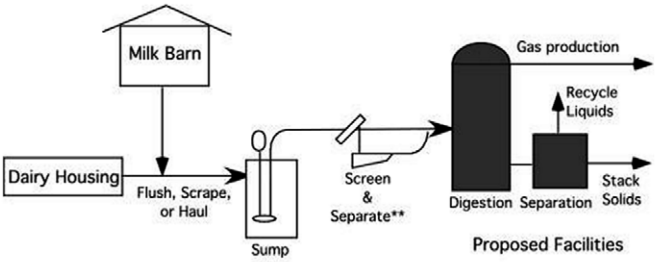

Fig. 1. Integration of anaerobic digestion system [7]

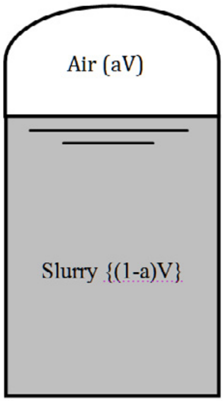

Fig. 2. V liters biogas digester

In the V liters digester, the gas space volume will be aV liters, where a is the gas space volume fraction in the digester and V is the digester volume. The amount of air in the gas space (F, gmol) is calculated by ideal gas law, as follow:

$$F = n = \frac{P(aV)}{RT} \tag{2}$$

where F is the amount of air in the digester gas space in initial process (gmol) (in the ideal gas law the amount of gas is well known as n), P is the pressure of the system (atm), R is the ideal gas constant (0,082 lt.atm/gmol.K), and T is the temperature of the system (K).

The water vapor pressure is much less than the oxygen and nitrogen vapor pressure, so that the equilibrium in the system can be assumed as oxygen-nitrogen equilibrium only. Based on the air compotition, the oxygen fraction in the gas space in initial process, y_1', will be 0.2, and the nitrogen fraction, y_2', will be 0.8. It is assumed that the slurry is water so that the amount of slurry (L, gmol) can be calculated by multiplying the slurry volume {(1-a)V} with the water density (ρ_{H2O}), then deviding the multiplying result with water molecular weight (BM_{H2O}):

$$L = \frac{(1-a)V\rho_{H_2O}}{BM_{H_2O}} \tag{3}$$

Part of the oxygen and nitrogen will dissolve in the slurry. In equilibrium condition, the amount of air that is dissolved in the slurry is Lg (gmol), and the amount of remained air in the gas space is Vg (gmol). The equilibrium gas space oxygen mol fraction is y_1 and the equilibrium gas space nitrogen mol fraction is y_2. In the liquid phase, the equilibrium oxygen mol fraction is x_1, and the equilibrium nitrogen mol fraction is x_2. This equilibrium is illustrated in Figure 3, as follow:

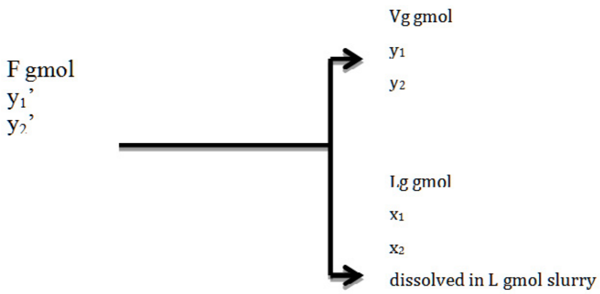

Fig. 3. Oxygen nitrogen gas-liquid equilibrium

Based on the schema in Figure 3, it can be arranged the total mass balance, oxygen mass balance, and nitrogen mass balance in the system, as follow:

$$F = Vg + Lg \tag{4}$$

$$F.y_1' = Vg.y_1 + (L + Lg)x_1 \tag{5}$$

$$F.y_2' = Vg.y_2 + (L + Lg)x_2 \tag{6}$$

The Henry's constant of oxygen, H_1, is 4.75 x 10^4 atm/mol fraction of oxygen dissolved in the water, and the Henry's constant of nitrogen, H_2, is 9.24 x 10^4 atm/mol fraction of nitrogen dissolved in the water [9]. The oxygen and nitrogen gas-liquid equilibrium correlations are written as:

$$x_1 = \frac{y_1.P}{H_1} \tag{7}$$

$$x_2 = \frac{y_2.P}{H_2} \tag{8}$$

The x_1 and x_2 in Equation 5 and 6 is substituted with x_1 and x_2 values from Equation 7 and 8. Rearrangement of Equation 5 and 6 result the equation to calculate y1 and y_2 as follow:

$$y_1 = \frac{H_1.(F.y_1')}{H_1.Vg + (L + Lg)P} \tag{9}$$

$$y_2 = \frac{H_2.(F.y_2')}{H_2.Vg + (L + Lg)P} \tag{10}$$

As the gas phase is consisted of oxygen and nitrogen only, the sum of oxygen mol fraction and nitrogen mol fraction in the gas phase will be 1, and be written in Equation 11, as follow:

$$y_1 + y_2 = 1 \tag{11}$$

The y_1 and y_2 values are obtained by trial and error, begining with try the Vg/F value, then solve Equation 4, 9, and 10 simultaniously until it is got the sum of y_1 and y_2 approximately of 1 according to Equation 11. The x_1 dan x_2 values are determined by substitutes y_1 and y_2 in Equation 7 and 8 with y_1 and y_2 values from equation 9 and 10. From the x_1 value obtained, the oxygen concentration in the slurry phase in the equilibrium condition, C_1 (mg/L), can be calculated by Equation 12, as follow:

$$C_1 = \frac{x_1(L + Lg)BM_{O_2}}{(1-a)V} x1000 \tag{12}$$

The analysis in this research is done by calculate the equilibrium oxygen concentration in the liquid/slurry phase in various gas space volume fraction in the digester, and then compare the values obtained with the oxygen methanogenic inhibition limit so that it can be seen the possibility the happen of oxygen methanogenic inhibition in the system.

3. Discussions

The oxygen methanogenic inhibition will possibly happen in the biogas production process if the oxygen concentration value in the slurry is higher than the methanogenic inhibition limit. From the calculation using Equation 2-12, there are got the amount of air in the gas space in initial process (F), the amount of air in the gas and slurry phase in equilibrium condition (Vg and Lg), and the equilibrium oxygen concentration in the slurry (C_1) in various gas space volume fraction in the digester, as be presented in Table 1 and Figure 5.

The equilibrium oxygen concentrations in the slurry in a from 0.1 to 0.9 are between 6.7 and 7.5 mg/L (Table 1 and Figure 4), much higher than the methanogenic inhibition limit according to Deublin and Steinhauser (2008) about 0.1 mg/L [4]. This phenomenon indicates that the methanogenic inhibition caused by the present of oxygen (air) in initial process can happen in all of gas space volume fraction in the biogas digester. However, the charts of the correlation of F and Vg with a are almost coincides (Figure 5), show that the remained air in the gas phase in equilibrium condition is just little less than the amount of air in the gas space in initial process and the dissolved oxygen in the slurry is very little. This little amount of oxygen has made possible to cause the oxygen methanogenic inhibition because methanogenic bacteria is very sensitive with the present of free molecular oxygen [6, 2].

Figure 4 show that the equilibrium oxygen concentration in the slurry will increase with the increasing of a, indicating the higher possibility the happen of oxygen methanogenic inhibition by the larger of gas space volume in the digester. The oxygen concentration in the slurry is in equilibrium with the oxygen partial pressure in the gas space. By the increasing of gas space volume fraction, the amount of air in the digester will increase and the amount of slurry in the digester will decrease. The great oxygen in the gas space will direct the equilibrium to the liquid phase, and by the less of the slurry volume the oxygen concentration in the slurry will be higher.

Table 1. F, Vg, Lg and C_1 value in various gas space volume fraction

a	F, V gmol	Vg, V gmol	Lg, V gmol	C_1, mg/L
0.10	0.00407	0.00343	0.00063	6.7855
0.15	0.00610	0.00550	0.00060	7.0339
0.20	0.00813	0.00756	0.00057	7.1652
0.30	0.01220	0.01169	0.00051	7.2943
0.40	0.01626	0.01583	0.00043	7.3620
0.50	0.02033	0.01999	0.00034	7.3959
0.60	0.02439	0.02411	0.00029	7.4298
0.70	0.02846	0.02824	0.00021	7.4495
0.80	0.03252	0.03238	0.00014	7.4644
0.90	0.03659	0.03652	0.00007	7.4760

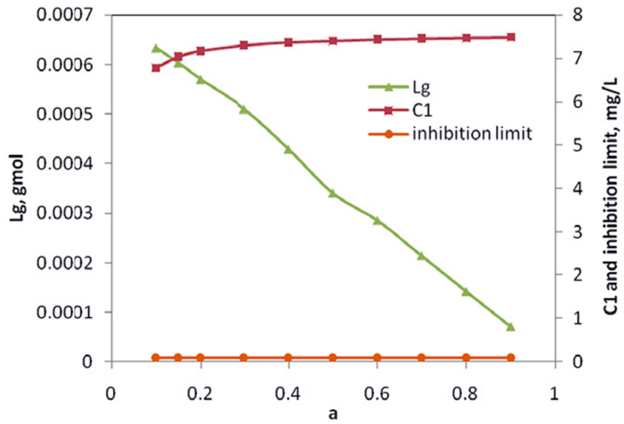

Fig. 4. The correlation of Lg and C_1 with a

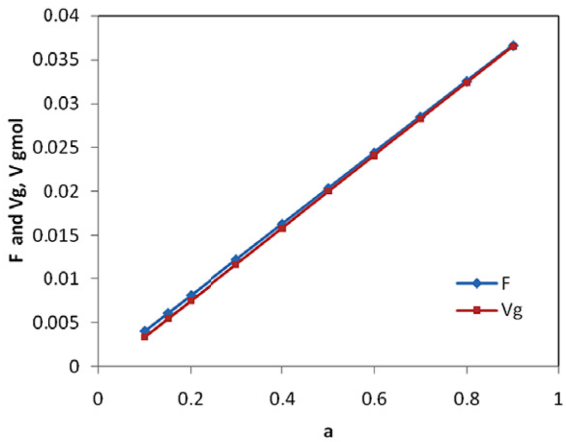

Fig. 5. The correlation of F and Vg with a

However, Figure 4 and 5 show that the amount of air that is dissolved in the slurry phase will decrease by the increasing of a. This trends may happen caused by the less of slurry volume in the greater of a. High light that the equilibrium oxygen and nitrogen partial pressure in the gas phase is not significant different in various of a, caused by the little oxygen and nitrogen solubility in the liquid phase. This little solubility also cause the little differences of the equilibrium oxygen concentration in the slurry in various of a. By the decreasing of slurry volume, the air that is dissolved in the slurry will decrease too.

4. Conclusions

Calculation results show that the equilibrium oxygen concentrations in all of gas space volume fraction in the digester are much higher than the methanogenic inhibition limit indicating the possibility the happen of the methanogenic inhibition in the system. The possibility of the methanogenic inhibition will be higher by the greater of gas space volume fraction in the digester.

5. Suggestion

The existence of facultative anaerobic bacteria in the biogas process may consume the oxygen in the slurry immediately so that the overall condition in the digester will be anaerobic in a certain time. Therefore, it is needed the experiments to study the real effect of oxygen removal in initial process to know how significant the effect on the biogas production process.

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